

What Is Claimed:

1. A solid oxide fuel cell comprising:
 - (a) a solid electrolyte comprised of an electronic insulator which allows transfer of anions, a ceramic-metal composite anode and a cathode;
 - (b) a fuel comprising a sulfur-containing hydrocarbon having a sulfur content of from about 1 ppm to about 5000 ppm; and
 - (c) an oxygen source.
2. The fuel cell according to claim 1, wherein the hydrocarbon is a petroleum distillate.
3. The fuel cell according to claim 2, wherein the petroleum distillate is selected from the group consisting of gasoline, diesel oil, naphtha, JP-4, JP-5, JP-8, kerosene, motor oil, natural gas, fuel oil and mixtures thereof.
4. The fuel cell according to claim 3, wherein the petroleum distillate is selected from the group consisting of JP-4, JP-5, JP-8 and mixtures thereof.
5. The fuel cell according to claim 3 wherein the petroleum distillate is selected from the group consisting of naphtha, kerosene, fuel oil and mixtures thereof.

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6. The fuel cell according to claim 3, wherein the petroleum distillate is selected from the group consisting of gasoline, diesel oil, natural gas and mixtures thereof.
 7. The fuel cell according to claim 2, wherein the hydrocarbon comprises an alcohol.
 8. The fuel cell according to claim 7, wherein the alcohol is selected from the group consisting of methanol, ethanol and mixtures thereof.
 9. The fuel cell according to claim 2, wherein the hydrocarbon is selected from the group consisting of dry methane, butane, toluene, decane and mixtures thereof.
 10. The fuel cell according to claim 1, wherein the sulfur-containing hydrocarbon fuel has a sulfur content of from about 1 ppm to about 1000 ppm.
 11. The fuel cell according to claim 10, wherein the sulfur-containing hydrocarbon fuel has a sulfur content of from about 10 to about 1000 ppm.
 12. The fuel cell according to claim 11, wherein the sulfur-containing hydrocarbon fuel has a sulfur content of from about 20 to about 1000 ppm.
 13. The fuel cell according to claim 12, wherein the sulfur-containing hydrocarbon fuel has a sulfur content of from about 100 ppm to about 1000 ppm.
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14. The fuel cell according to claim 13, wherein the sulfur-containing hydrocarbon fuel has a sulfur content of from about 250 ppm to about 1000 ppm.
15. The fuel cell of claim 1, wherein the solid electrolyte is an oxide ion conducting material.
16. The fuel cell of claim 15, wherein the oxide ion conducting material is selected from the group consisting of doped ceria, doped zirconia and doped lanthanum gallate.
17. The fuel cell of claim 16, wherein the doped ceria is selected from the group consisting of gadolinium doped ceria, samarium-doped ceria and yttria-doped ceria.
18. The fuel cell of claim 15, wherein the oxide ion conducting material is yttria-doped zirconia.
19. The fuel cell of claim 16, wherein the doped zirconia is scandium-doped zirconia.

20. A process of producing electrical energy, comprising:
- (a) providing a solid oxide fuel cell comprising a solid electrolyte that is an electronic insulator which allows transfer of anions, a ceramic metal composite anode and a cathode;
 - (b) contacting said cathode with an oxygen source; and

- (c) contacting said anode with a fuel comprising a sulfur-containing hydrocarbon having a sulfur content of from about 1ppm to about 5000 ppm.

21. The process according to claim 20, wherein the hydrocarbon is a petroleum distillate.
22. The process according to claim 21, wherein the petroleum distillate is selected from the group consisting of gasoline, diesel oil, naphtha, JP-4, JP-5, JP-8, kerosene, motor oil, natural gas, fuel oil and mixtures thereof.
23. The process according to claim 22, wherein the petroleum distillate is selected from the group consisting of JP-4, JP-5, JP-8 and mixtures thereof.
24. The process according to claim 22, wherein the petroleum distillate is selected from the group consisting of naphtha, kerosene, fuel oil and mixtures thereof.
25. The process according to claim 22, wherein the petroleum distillate comprises gasoline.
26. The process according to claim 22, wherein the petroleum distillate comprises diesel oil.

27. The process according to claim 20, wherein the hydrocarbon is selected from the group consisting of alcohols, dry methanes, butane, toluene, decane and mixtures thereof.

5 28. The process according to claim 27, wherein the hydrocarbon comprises an alcohol.

29. The process according to claim 28, wherein the alcohol is selected from the group consisting of methanol, ethanol and mixtures thereof.

30. The process according to claim 20, wherein the sulfur-containing hydrocarbon has a sulfur content of from about 10 ppm to about 1000 ppm.

31. A method of restoring the operability of a solid oxide fuel cell comprising a solid electrolyte comprised of an electronic insulator which allows transfer of anions, a ceramic-metal alloy composite anode and a cathode and which was deactivated by sulfur poisoning, said method comprising the step of heating the anode in a mixture containing steam.

32. A method according to claim 31, wherein the anode is heated in a gaseous mixture comprising steam.

33. A method according to claim 31, wherein the anode is heated at between about 600°C and about 800°C for a period of about one (1) hour to about three (3) hours.

34. A method of fabricating a porous cermet as a direct-oxidation anode material for a solid-oxide fuel cell, said method comprising:

- (a) providing a porous nickel-containing cermet, with Ni content between 10% and 60%;
- (b) contacting said cermet with a leaching agent to remove at least a portion of said nickel, thereby imparting additional porous character to said cermet;
- (c) contacting said porous cermet with an impregnant comprising a soluble copper salt, thereby depositing said copper salt in the pores of said cermet;
- (d) calcining the copper salt-impregnated cermet at a temperature sufficient to convert said copper salt to copper oxide; and
- (e) reducing said copper oxide to elemental copper, thereby producing said direct-oxidation anode material.

35. The method of claim 34, wherein in step (b) all of the nickel is leached from said cermet.

36. The method according to claim 34, wherein in step (b) between about 50% and about 99% of the nickel is leached from said cermet.

37. The method of claim 36, wherein the cermet is impregnated with a soluble copper salt, which yields an amount of elemental copper that is approximately equivalent to the weight of elemental nickel leached from the cermet in step (b).

38. The method of claim 34 which comprises the further step of treating the direct-oxidation anode material with a cerium salt, which is converted to cerium oxide.

39. A method of fabricating a porous, multi-layer ceramic laminate as a direct oxidation anode with supported electrolyte structure for a solid-oxide fuel cell, said laminate comprising at least a first layer and a second layer, the second layer being relatively dense in comparison to the first layer, said method comprising:

- (a) preparing a first formulation in the form of a slurry comprising a binder, a carrier medium and a ceramic powder, at least a portion of said ceramic powder including nickel oxide and YSZ;
- (b) forming said slurry into a first layer;
- (c) preparing a second formulation in the form of a slurry comprising a binder, a carrier medium, and YSZ;
- (d) forming said slurry into a second layer;
- (e) forming an assemblage comprising said layer and said second layer, superposed one upon the other, thereby providing a laminate preform;
- (f) heating said laminate preform to a temperature sufficient to sinter said ceramic powder;
- (g) reducing at least a portion of the nickel oxide present in said sintered laminate to elemental nickel;
- (h) contacting said sintered laminate with a leaching agent to remove at least a portion of said nickel thereby imparting a porous character to the first layer of said sintered laminate;

- (i) contacting the first layer of said sintered laminate with an impregnant comprising soluble copper salt, thereby depositing said salt in the pores of said sintered laminate;
- (j) calcining the copper salt impregnated sintered laminate at a temperature of at least 600°C, thereby converting said copper salt to copper oxide; and
- (k) reducing said copper oxide to elemental copper, thereby producing said direct-oxidation anode with supported electrolyte structure.

40. A method of fabricating a porous, multi-layer ceramic laminate as a direct oxidation anode with supported electrolyte structure for a solid-oxide fuel cell, said laminate comprising at least a first layer and a second layer, the second layer being relatively dense in comparison to the first layer, said method comprising:

- (a) preparing a first tape formulation in the form of a slurry comprising a binder, a carrier medium and a ceramic powder, at least a portion of said ceramic powder including nickel oxide and YSZ;
- (b) forming said slurry into a first tape;
- (c) preparing a second tape formulation in the form of a slurry comprising a binder, a carrier medium, and YSZ;
- (d) forming said slurry into a second tape;
- (e) forming an assemblage comprising said first anode tape and said second electrolyte tape, superposed one upon the other, thereby providing a laminate preform;

- (f) heating said laminate preform to a temperature sufficient to sinter said ceramic powder;
- (g) reducing at least a portion of the nickel oxide present in said sintered laminate to elemental nickel;
- 5 (h) contacting said sintered laminate with a leaching agent to remove at least a portion of said nickel thereby imparting a porous character to the first layer of said sintered laminate;
- (i) contacting the first layer of said sintered laminate with an impregnant comprising soluble copper salt, thereby depositing said salt in the pores of said sintered laminate;
- (j) calcining the copper salt impregnated sintered laminate at a temperature of at least 600C°, thereby converting said copper salt to copper oxide; and
- (k) reducing said copper oxide to elemental copper, thereby producing said direct-oxidation anode with supported electrolyte structure.

41. A method of fabricating a porous, multi-layer ceramic laminate as a direct oxidation anode with supported electrolyte structure for a solid-oxide fuel cell, said laminate comprising at least a first layer and a second layer, the second layer being relatively dense in comparison to the first layer, said method comprising:

- 20 (a) preparing a first tape casting formulation in the form of a slurry comprising a binder, a carrier medium and a ceramic powder, at least a portion of said ceramic powder including nickel oxide and YSZ;

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- (b) applying the slurry of said first tape casting formulation to a supporting substrate and forming said slurry into a first tape;
- (c) preparing a second tape casting formulation in the form of a slurry comprising a binder, a carrier medium, and YSZ;
- 5 (d) applying the slurry of said second tape casting formulation to a supporting substrate and forming said slurry into a second tape;
- (e) forming an assemblage comprising said first anode tape and said second electrolyte tape, superposed one upon the other, thereby providing a laminate preform;
- (f) heating said laminate preform to a temperature sufficient to sinter said ceramic powder;
- (g) reducing at least a portion of the nickel oxide present in said sintered laminate to elemental nickel;
- (h) contacting said sintered laminate with a leaching agent to remove at least a portion of said nickel thereby imparting a porous character to the first layer of said sintered laminate;
- (i) contacting the first layer of said sintered laminate with an impregnant comprising soluble copper salt, thereby depositing said salt in the pores of said sintered laminate;
- 20 (j) calcining the copper salt impregnated sintered laminate at a temperature of at least 600°C, thereby converting said copper salt to copper oxide; and
- (k) reducing said copper oxide to elemental copper, thereby producing said direct-oxidation anode with supported electrolyte structure.

42. The method of claim 41, wherein the slurry of said second tape casting formulation is applied to said first tape, thereby forming the anode and electrolyte.
43. The method of claim 41, wherein in step (h) substantially all of the nickel is leached from the sintered laminate.
44. The method according to claim 41, wherein in step (h) between about 50% and about 99% of the nickel is leached from the sintered laminate.
45. The method of claim 44, wherein the laminate is impregnated with a soluble copper salt which yields an amount of elemental copper that is approximately equivalent to the weight of elemental nickel leached from the laminate in step (h).
46. The method of claim 41 which comprises the further step of treating the direct oxidation anode with supported electrolyte structure with a cerium salt, which is converted to cerium oxide.
47. The method of claim 41, wherein the first tape casting formulation further comprises an organic pore forming agent.
48. The method of claim 47, wherein said organic pore forming agent comprises powdered graphite.

49. The method of claim 41, wherein said leaching agent selectively dissolves nickel with no appreciable dissolution of YSZ.

50. The method of claim 49, wherein said leaching agent is heated nitric acid.

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51. The method of claim 41, further comprising, prior to sintering:

- (a) preparing a third tape casting formulation in the form of a slurry comprising a binder, a carrier and a ceramic powder, the coefficient of thermal expansion of said ceramic powder, when sintered, being compatible with that of sintered YSZ;
- (b) applying the slurry of said third tape casting formulation to a supporting substrate and forming said slurry into a third tape, the thickness of said third tape being relatively greater than the thickness of said second tape;
- (c) perforating said third tape, thereby forming at least one aperture through the thickness of said tape; and
- (d) superposing said perforated third tape on said laminate preform in contact with said first tape.

52. The method of claim 51, wherein said at least one aperture in said third tape has a periphery with a continuously curved outline.

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53. The method of claim 41, wherein, after sintering, contacting of the first layer of said sintered laminate with said impregnant is effected by passing said impregnant through said at least one aperture in said third tape.

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